

## Study the Influence of Alkaline and Acid Treatments on Surface Area and Porosity for a Mixture of Clays by Physical Adsorption of N<sub>2</sub> Gas

Saba Adil Saed, Dunya Edan - AL-Mammar

Department of Chemistry, College of Science, University of Baghdad, Baghdad, Iraq

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### Abstract:

The specific surface area and porosity for a mixture of illite, kaolinite and chlorite clays from Zorbatiya region east of Iraq, are investigated in this study, before and after modification by physical adsorption of N<sub>2</sub> gas at 77 K. The modifications carried out by using hydrochloric acid HCl, sulfuric acid H<sub>2</sub> SO<sub>4</sub> and alkaline modification with sodium hydroxide NaOH. Nitrogen desorption/adsorption isotherms at 77 K are recorded to determine the values of the N<sub>2</sub> adsorbed corresponding to the formation mono-layer, specific surface area  $S_{BET}$ , total pore volume and mean pore diameter by using the Brunauer -Emmett and Teller (BET) equation. Langmuir adsorption isotherm model also used to calculate the mono-layer capacity, Langmuir constant and surface area for Langmuir model  $S_{Lang}$ , for different samples. t-plot method was used to give information about specific surface area  $S_t$  and roll type of pores in the system by plotting the values of the experimented volumes of adsorbed nitrogen gas  $V_a$  (cm<sup>3</sup> STP/g) against the statistical thickness  $t$ . Barrett - Joyner – Halenda (BJH) was applied to pore –size determines on the basis of a kelvin equation.

**Key words:** RC, R-HCL, R-H<sub>2</sub> SO<sub>4</sub> , R-NaOH, BET, Langmuir plot, t-plot, BJH-plot.

### Introduction:

Adsorbents materials are mainly an important elements in the adsorption sampling devices that estimate the values of capacities for samplers of the airborne vapors. Porous adsorbents substances such as: alumina, silica gel, active carbon, porous-polymer and clays are generally used in samplers for the organic vapors, since they have a large specific surface areas and micropore structures that effective for the vapors adsorption. The affinity of the adsorbents to gases depended on the physical adsorption mechanisms, and large surface areas thus bring about a large adsorption capacity, and micro-pores are sufficient in adsorbing the gases at low concentrations by capillary condensation [1]. Gas adsorption in porous media attracts a great deal of attention because it is entered in a large wide of industrial process such as separation, catalysis and purification. At low temperature of the measurements of adsorption to some fluids such as: nitrogen and argon gas are largely applied for characterization of porous solids, amounts of adsorbed materials and capillary condensation / evaporation pressures are belong to the geometrical features for the porous matrix [2]. For examples, the specific surface area for the porous substances is generally assessed from experiments of adsorption (previous to capillary-condensation for a fluid) on the basis of the BET (Brunauer-Emmett-Teller) equation in which the fluid is suppose to cover the pore walls uniformly [3].The t-plot method is also an important parameter to describe the capillary condensation by plotting the values of volumes of the N<sub>2</sub> gas that adsorbed on the surfaces of the samples as a function of the statistical –thickness of the adsorbed layer [4]. In BJH (Barrett-Joyner-Helenda) method, the pore size distribution is calculated from the adsorption isotherm by using kelvin equation [5]. The aim of this study to present simulation results for N<sub>2</sub> adsorption at 77 K in porous clay samples, also discuss the validity of BET, Langmuir, t-plot and BJH methods to assess a specific surface area and pore size distribution from N<sub>2</sub> adsorption data.

### Experimental:

The raw clay (RC) comes from region of Zorbatiya at Al- Mukdadiya city, Iraq. The main composition is shown in Table 1.

**Table 1:** Chemical composition for the RC sample.

component	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	Cl	MnO	LOI
Wt%	19.60	3.80	4.50	15.20	3.40	1.30	12.80	0.60	0.10	1.20	14.80	0.38	19.60

The analysis done for the RC indicates that this clay was a mixed of three types of clay including kaolinite, illite and chlorite.

**Clay preparation:**

30 g of pretreated clay was mixed with 100 ml distilled water and shaken for one hour at room temperature then filtered by using Buckner funnel, then dried at 120°C in an oven for seven hours, cooled and stored in a desiccator. Activation with acid was carried out by using 37% hydrochloric and 98% sulfuric acids while the alkaline treated was performed by using sodium hydroxide.

**RC activated with HCl (R-HCl):**

20 g RC was stirred with a volume of 67 ml from 0.25 M HCl a thermostatic shaker type (Gallen Kamp, England) at room temperature for two hours, then allowed to settle for one hour and filtered by Buchner funnel. The precipitated was washed many times with distilled water until the pH equal to 7, then dried at 120°C for two hours. The product clay was calcinated by using muffle furnace type (BS32C, Korea) at 750 °C for 4 hours, the obtained clay labeled as R-HCl.

**RC activated with H<sub>2</sub> SO<sub>4</sub> (R-H<sub>2</sub> SO<sub>4</sub>):**

20 g of RC was mixed with 200 ml volume from 0.25 M H<sub>2</sub> SO<sub>4</sub> in a shaking water bath for six hours at 70°C, then allowed to stabilizes for fourteen hours. The produce clay was filtered and washed many times with distilled water till it reaches pH 7. Finally the sample dried for two hours at 120°C and calcinate at 750°C for 4 hours, the obtained clay marked as R-H<sub>2</sub> SO<sub>4</sub> .

**RC treatment with NaOH (R-NaOH):**

A volume of 70 ml from (5M) NaOH was added to five grams pretreated raw clay under 800 rpm mechanical stirring for 4 hours to yield a homogenous suspension, by using centrifugation at 5000 rpm, the product was separated, washed with distilled water several times and dried at 105°C for 4 hours. The result sample marked as R-NaOH.

The specific surface area and porosity is determined by nitrogen adsorption-desorption isotherms at 77 K by using BELSORP-miniII (High precision surface area and pore size Analyzer, Spain). The values of  $S_{BET}$  for the different samples are estimated by using Brunauer-Emmett and Teller (BET equation). The total pore volumes are calculated from the volume of liquid nitrogen held at the relative  $P$  ( $P/P^{\circ} = 0.95$ ) and the micropore volume are calculated by using t-plot method.

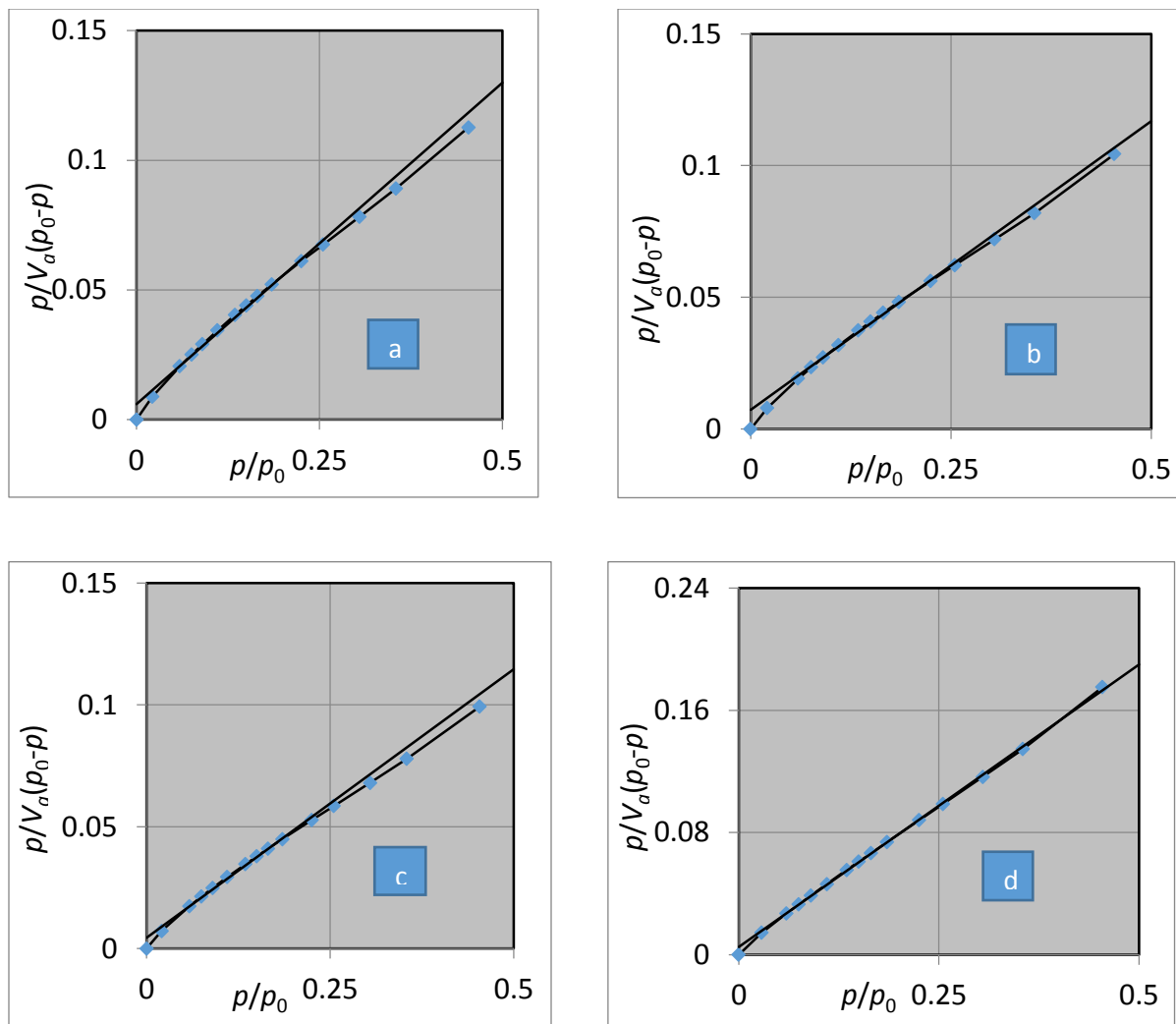
**Results and discussion:**

The characteristic and the adsorption capacity for the samples could be predicted from the surface area and porosity information. The change of crystal structure can be examined from the changes of pore texture parameters.

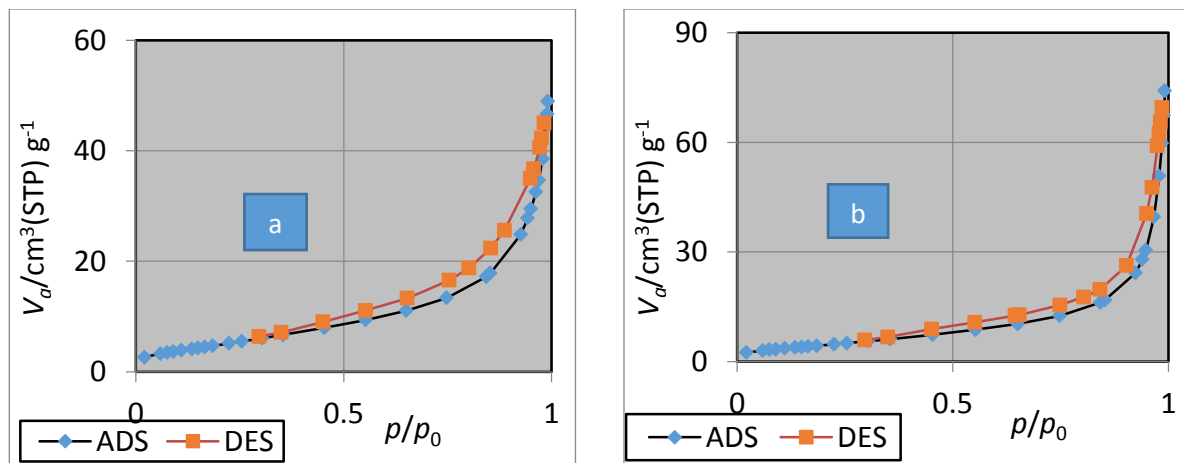
The BET equation is mostly used in the field of characterization the porous substances, by determining of specific surfaces from the adsorption isotherm on the basis of that, this model improved to describe multi-layer adsorption. The most assumption of this model is that, adsorption occurs at homogenous surface sites that have the same energy and the molecules may be adsorbed on each other, so the adsorption energy for all molecules that adsorbed above the first layer is equal to the energy of the bulk liquid. The BET equation was given by [6].

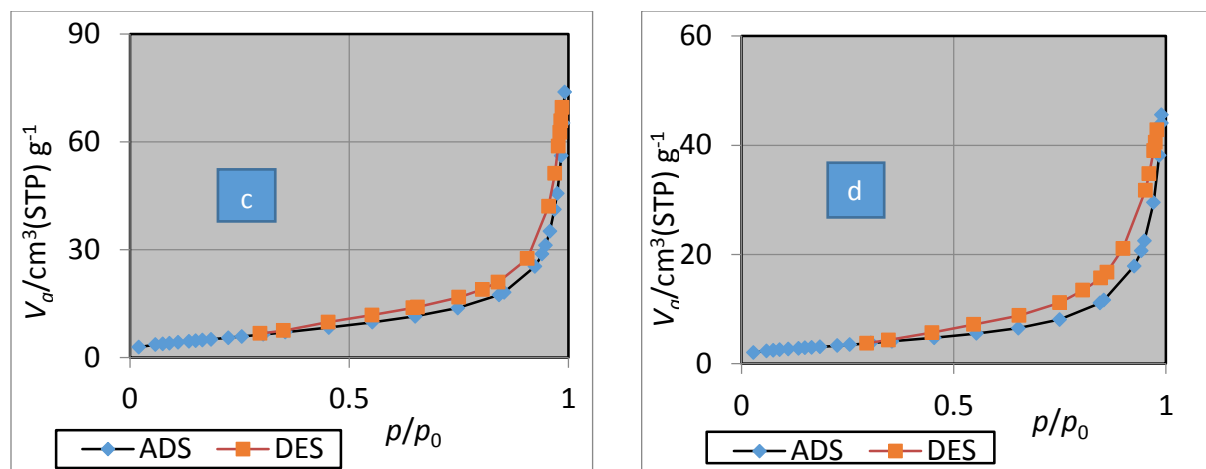
$$\left[ \frac{1}{V} \right] \frac{P/P^{\circ}}{(1-P/P^{\circ})} = \left[ \frac{1}{V_m C} \right] + \left[ \frac{C-1}{V_m C} \right] P/P^{\circ} \text{----- (1)}$$

Where  $V$ : is the volume of the adsorbate under pressure  $P$ ,  $P^{\circ}$ : The saturated vapor pressure of the gas,  $V_m$ : The volume of the gas adsorbed needed to formation mono-layer,  $C$ : is BET constant for the given adsorbate, it given by :  $C = \exp[(E_1 - E_0)/ RT]$ , where  $R$ : Gas constant,  $T$ : Temperature,  $E_1$ : Enthalpy of adsorption for the first layer,  $E_0$ : The enthalpy of liquefaction for the adsorbate. The values of  $V_m$  and  $C$  can be calculated from the intercept and the slop of BET plots as given in Figure 1. The specific surface area was estimated by using BET equation, the  $N_2$  - desorption – adsorption isotherms at 77 K for the clay samples surfaces are represented in Figure 2 (a, b, c and d)



**Figure 1:** BET plots for N<sub>2</sub> gas adsorption isotherms at 77K onto: (a) RC, (b) R-HCl, (c) R-H<sub>2</sub> SO<sub>4</sub> and (d) R-NaOH.





**Figure 2:** Nitrogen gas adsorption-desorption isotherms for: (a) RC, (b) R-HCl, (c) R-H<sub>2</sub> SO<sub>4</sub> and (d) R-NaOH.

Hysteresis loop are noticed on these isotherms, which can be classified as type H3 hysteresis loop according to IUPAC classification. This type indicate the presence of plaque-like meso-pores with spaces showed between parallel plates [7], on the other hand the presence of a hysteresis loop pointed to type IV according to IUPAC classification, but there is either no plateau behavior for this type or it is so difficult to notice because it reduced to almost one point.

The adsorption-desorption branched joined at a relative pressure  $P/P^0$  approximately equal to 0.35 for RC, R-HCl, R-H<sub>2</sub> SO<sub>4</sub> and R-NaOH, which indicates the existence of a small amount of micro-pores. The N<sub>2</sub> gas adsorption was sharply increased at a higher relative pressure due to the capillary – condensation phenomenon of N<sub>2</sub> gas in the meso-pores, and-or macro-pores and its multi-layer adsorption onto macro-pores and meso-pores. The type H3 hysteresis loop at higher  $P/P^0$  was observed, showing the presence of macro-pores and or meso-pores [8]. Also it was concluded that the pores in the clay samples are a narrow and slit-like shaped pores or aggregates of a plate-like particles also will be drawn [9].

Table 2 shows the BET specific surface area for the adsorption of N<sub>2</sub> onto clay samples that calculated from BET graphs for N<sub>2</sub> adsorption isotherm at 77 K, Figure 1 (a, b, c and d). It is obvious that the  $S_{BET}$  values increased from 17.153 for RC to 19.215 and 19.37 m<sup>2</sup>/g for the R-HCl and R-H<sub>2</sub> SO<sub>4</sub> respectively and reduced to 11.607 m<sup>2</sup>/g for NaOH. Mean pore diameter increased from 15.145 nm for RC to 24.665, 22.662 and 24.18 nm for R-HCl, R-H<sub>2</sub> SO<sub>4</sub> and R-NaOH, while the total pore volume that estimated from liquid volume of N<sub>2</sub> gas at high relative pressure ( $P/P^0$ ) near unity 0.99, were reduced from 0.1097 for RC to 0.1058, 0.0727 and 0.0701 cm<sup>3</sup>/g for R-HCl, R-H<sub>2</sub> SO<sub>4</sub> and R-NaOH. The values of  $C$ , the BET constant revealed to enthalpy of the adsorption increased from 31.18 for RC to 41.9, 51.11 and 73.66 for R-HCl, R-H<sub>2</sub> SO<sub>4</sub> and R-NaOH and the values of the mono layer volume  $V_m$  according to the BET equation increased from 3.940 cm<sup>3</sup>/g for RC to 4.414, 4.450 cm<sup>3</sup>/g for R-HCl, R-H<sub>2</sub> SO<sub>4</sub> and reduced for R-NaOH to 2.666 cm<sup>3</sup>/g.

**Table 2:** Nitrogen gas adsorption isotherm data for RC and activated clays with acids and NaOH.

BET plot							Langmuir plot			t- plot
	$V_m$ (cm <sup>3</sup> /g)	$S_{BET}$ (m <sup>2</sup> /g)	$C$	total pore volume (cm <sup>3</sup> /g)	mean pore diameter (nm)	$r_{p-peak}$ (area) (nm)	$v_m$ (cm <sup>3</sup> /g)	$S_{Lang}$ (m <sup>2</sup> /g)	$B$	$S_t$ (m <sup>2</sup> /g)
RC	3.940	17.153	31.18	0.1097	15.145	1.22	3.940	17.149	1.1162	13.407

R-HCl	4.414	19.215	41.90	0.1058	24.665	1.65	4.318	18.797	0.5496	14.390
R-H <sub>2</sub> SO <sub>4</sub>	4.450	19.37	51.11	0.0727	22.662	1.65	4.243	18.47	1.189	15.755
R-NaOH	2.666	11.607	73.66	0.07016	24.18	4.62	3.1444	13.686	0.6288	10.524

Langmuir-adsorption-isotherm written as [10].

$$P/a = \frac{1}{V_m} \cdot P + \frac{1}{B} \cdot \frac{1}{V_m} \text{-----} (2)$$

Where : P(Pa) is the pressure of the adsorbate at equilibrium.  $V_m$  (mol/g) the mono-layer capacity. a (mol/g) amount of the adsorbed gas. B is Langmuir adsorption isotherm constant. The values of  $V_m, B$  were estimated from slop and intercept of the plot between P/a vs. P.

Figure 3 (a, b, c and d) shows the Langmuir plots for N<sub>2</sub> adsorption isotherm onto RC, R-HCl, R-H<sub>2</sub> SO<sub>4</sub> and R-NaOH, it is clear from the values of mono layer capacity  $V_m$  calculated from Langmuir plots that it is an increase in this value by activation of clay by both HCl and H<sub>2</sub> SO<sub>4</sub> from 3.940 cm<sup>3</sup>/g for RC to 4.318 cm<sup>3</sup>/g for R-HCl and 4.243 cm<sup>3</sup>/g for R-H<sub>2</sub> SO<sub>4</sub> .

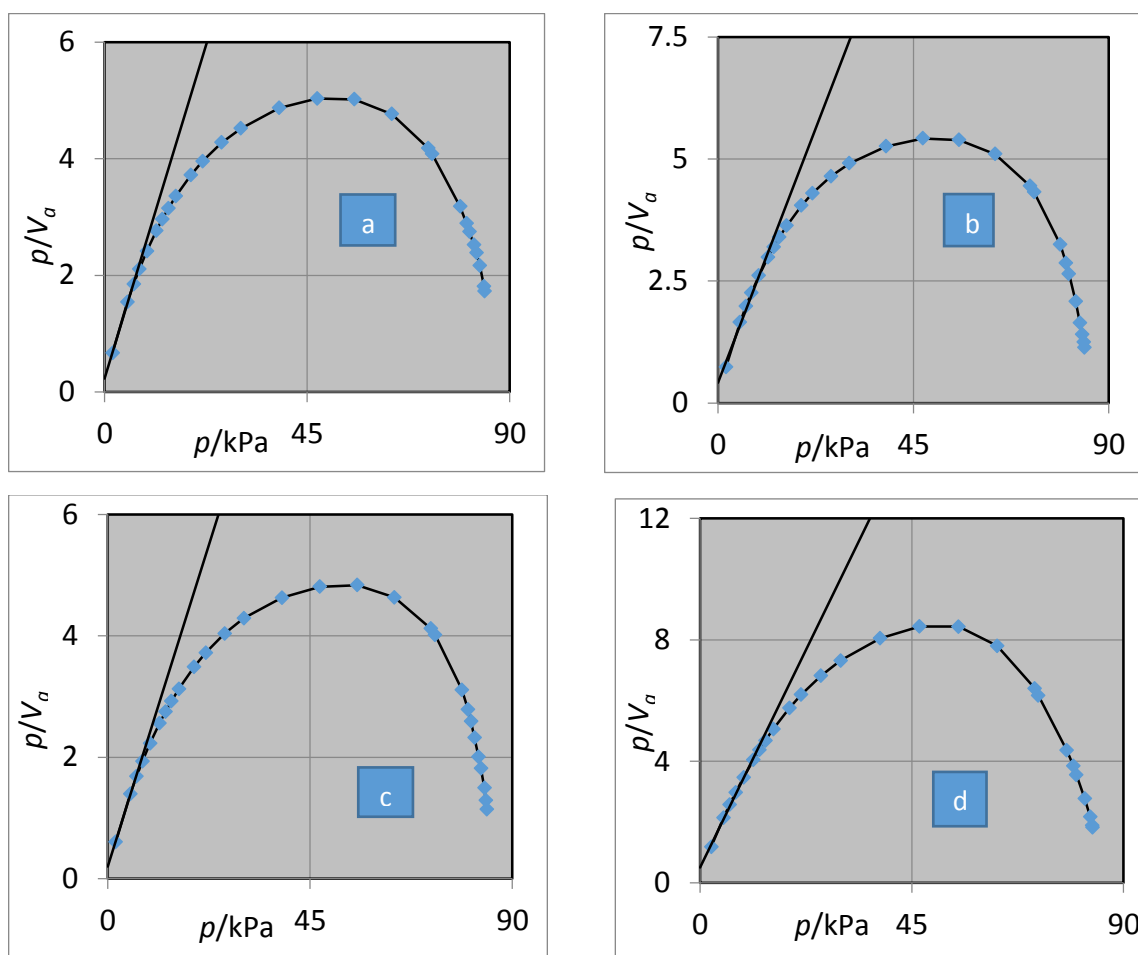


Figure 3: Langmuir plots for N<sub>2</sub> gas adsorption isotherms onto: (a) RC, (b) R-HCl, (c) R-H<sub>2</sub> SO<sub>4</sub> and (d) R-NaOH.

Furthermore the alkaline treated clay have less values of  $S_{BET}, V_m, V_m$  that the RC and acid activated samples, this may be related to that the alkaline treated affect the clay structure and leads to a passivation process, this involving partial blockage for the pores [11]. Acid may affect the chemical composition and structure of layered silicates

indifferent ways. The changes in crystal structure of the clay depended on the type of the layered silicate and the acid activation conditions such as the type of acid used, acid concentration and temperature [12]. Since it was increasing in the specific surface area with increase the values of  $V_m$ ,  $V_m$  this predicted that activation with both HCl and  $H_2 SO_4$  leads to an increase in the power and amount of the active centers on the surface (acid centers) [13].

**t- plot method:**

De-Boer [4] determined from their empirical studies the t-curve that gives a good picture for the whole pore system. The plot between the experimental values of the volume of  $N_2$  gas adsorbed in  $cm^3$  STP/g of adsorbent  $V_a$ , ( which are founded as a function of the relative pressure ) against the thickness of an adsorbate layer  $t$  that is typically referred to as the statistical thickness  $t$  for  $N_2$  [14]:

$$t^0_{(A)} = 3.54 \left[ \frac{5}{2.303 (\text{Log} \frac{p^0}{p})} \right] \text{-----} (3)$$

A straight line was gained goes through the origin point and its slop is represented the value of  $S_t$  surface area value, that obtained by the equation:

$$S_t = 15.47 [V_a/t] \text{-----} (4)$$

When 15.47 represents the conversion of the gas. Figure 4 (a, b, c and d) shows the V-t plots for  $N_2$  adsorption isotherms onto the different samples. The values of measured  $S_t$  listed in Table 2. It is clear from this table that the surface area  $S_t$  values for these samples ranged as:  $S_t$  R- $H_2 SO_4$  >  $S_t$  R-HCl >  $S_t$  RC >  $S_t$  R-NaOH.

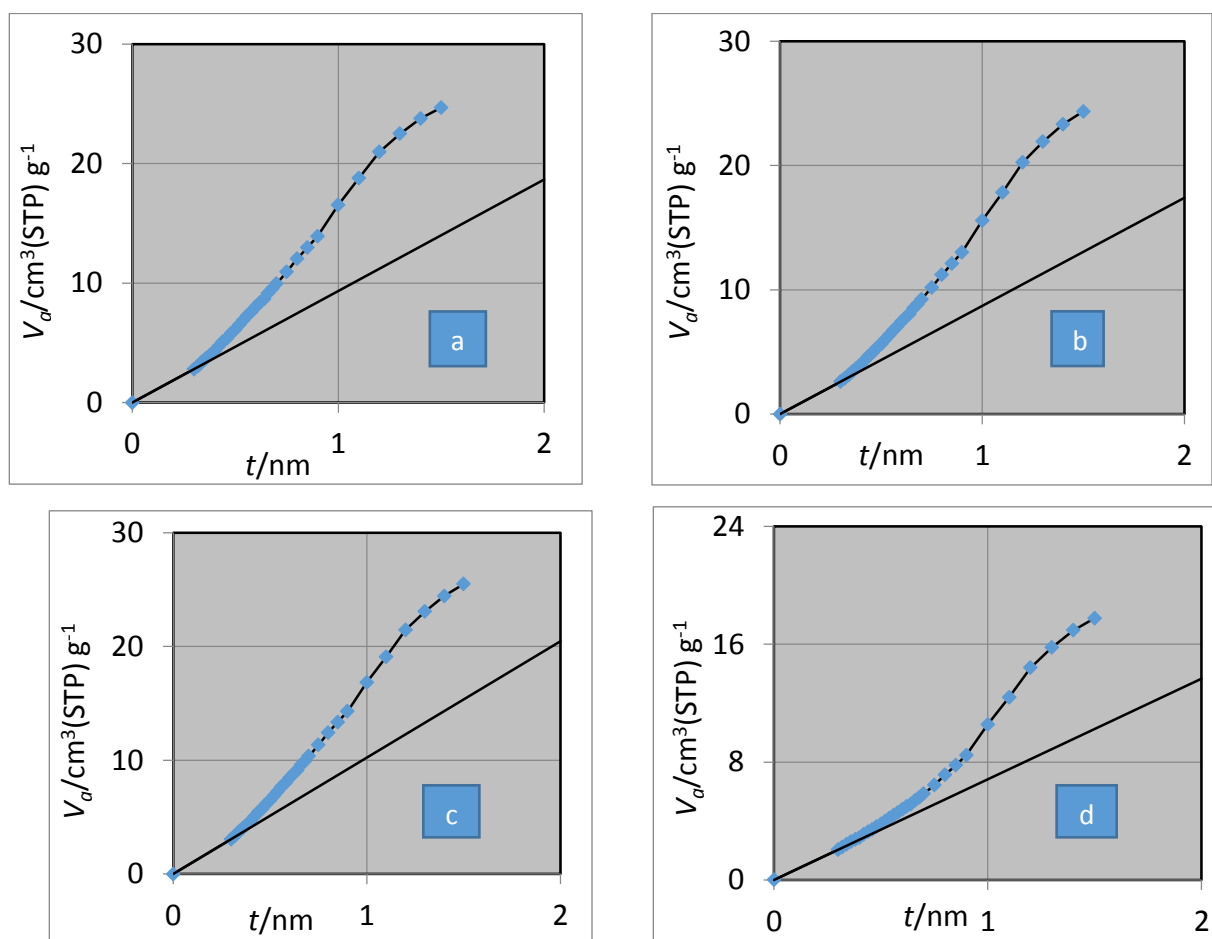


Figure 4: V-t plots for  $N_2$  gas adsorption isotherms onto: (a) RC, (b) R-HCl, (c) R- $H_2 SO_4$  and (d) R-NaOH.

The V-t plot shows the horizontal departures from the straight line that indicate the existence of micropores while the vertical plots point to the presence mesopores [15], this could be explained as: at a certain value of pressure capillary condensation phenomenon will occur in a pores that have certain dimensions and shapes, the adsorption branch lies above the t curve. The data obtained show a good agreement between the values of  $S_{BET}$ ,  $S_{Lang}$  and  $S_t$  for all samples, that may be related to the attendance of micropores in the texture of the clays.

**BJH-plot method:**

Although BJH method is build on idealized pores geometries it may deliver some information about mesoporosity. The pore size distribution was estimated using the standard BJH method with the kelvin equation [16].

$$r_K = 2\delta V_p / RT \ln \frac{p^0}{p} \text{----- (5)}$$

Where  $r_K$ : is kelvin radius °A,  $\delta$ : is the surface tension of the adsorbate,  $R$ : gas constant,  $T$ : temperature in kelvin,  $V_p$ : is the molar volume of the condensed liquid. The pore radius  $r_p$  is estimated by the equation:

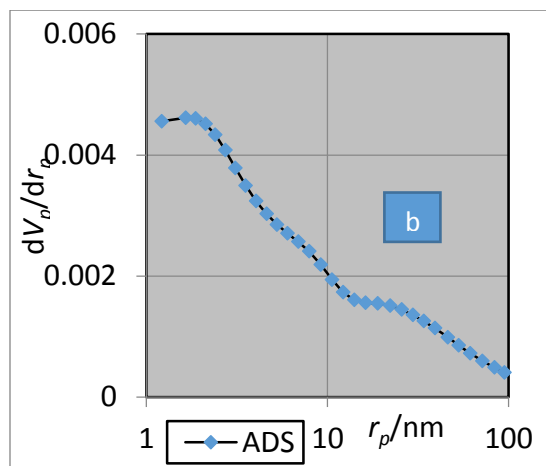
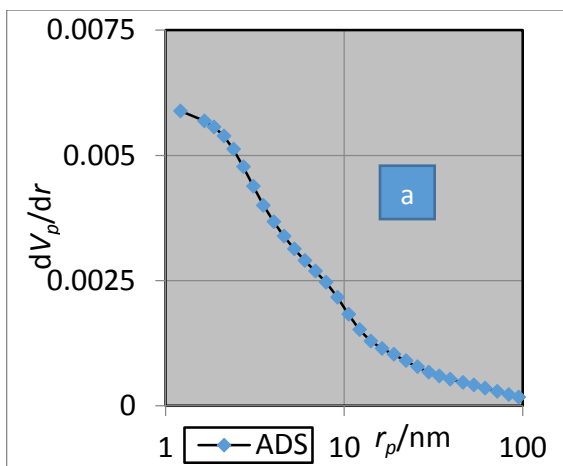
$$r_p = r_K + t \text{----- (6)}$$

Where t: is the statistical thickness of the N<sub>2</sub> gas on the pore wall at relative pressure. Table 3 shows the BJH-plot method data for the clay samples.

**Table 3:** BJH-plot method data for the clay samples

	$V_p$ (cm <sup>3</sup> /g)	$r_{p-peak}$ (area) nm	$Q_p$ (m <sup>2</sup> /g)
<b>RC</b>	0.074195	1.22	24.099
<b>R-HCl</b>	0.107300	1.65	23.005
<b>R-H<sub>2</sub> SO</b>	0.110800	1.65	24.755
<b>R-NaOH</b>	0.070379	4.62	13.693

Figure 5 (a, b, c and d) shows pore size distributions of porous clay samples, this figure shows that these clays have a uniform porosity  $r_{p-peak}$  equal to 1.22, 1.65 and 1.65 nm for the RC, R-HCl and R-H<sub>2</sub> SO<sub>4</sub> while 4.62 nm for the R-NaOH.



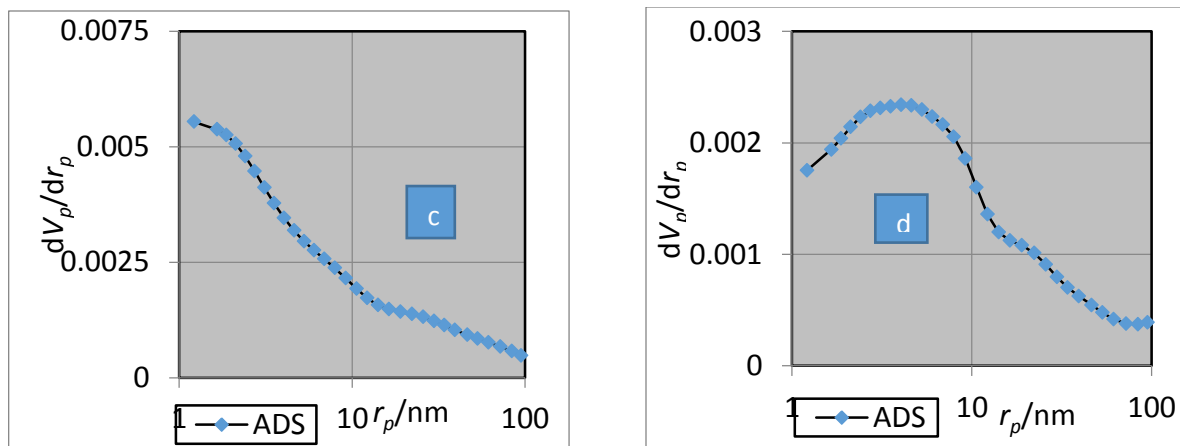


Figure 5: Pore size distributions of porous: (a) RC, (b) R-HCl, (c) R-H<sub>2</sub> SO<sub>4</sub> and (d) R-NaOH.

**Conclusion:**

Acid activation has been successfully introduced to improve the adsorption capacity for the mixed clay, than the alkaline treatment, this was observed by the highest values of layer volume  $V_m$  that showed a good agreement by using BET, Langmuir isotherm and t-plot methods. The observed increasing in the values of specific surface area according to the BET and Langmuir, adsorption isotherm point to that the activation with HCl and H<sub>2</sub> SO<sub>4</sub> leads to increase the amounts of the active acid centers on the clay surfaces. Adsorption isotherm type IV was represented with H3 type hysteresis loop which indicated to presence meso-pores, as well it is a characteristic of slit-like shape pore substances. The N<sub>2</sub> adsorption increase at high relative pressure suggested the occurrence of capillary – condensation phenomenon in the meso and or macropores with multi-layer adsorption onto these pores. The V-t plot shows a horizontal departures from the straight line that indicate the existence of micropores, while the vertical plots point to the presence of mesopores. BJH plot method shows that these clay samples have a uniform porosity, finally, this clay considered as a promise, inexpensive porous adsorbent.

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